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Study of Interaction Between Diffusion and Reaction in Short Contact Time Catalytic Partial Oxidation: Comprehensive Modeling of A Packed-Bed Reactor with Detailed Kinetics

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Highlights

- Adiabatic packed-bed reactor model was proposed that explicitly accounts for diffusion limitations
- Microkinetics allowed assessing the model in a wide operating range
- Influence of catalyst descriptors on reactor performance was studied
- Effect of homogeneous combustion on product distribution was investigated at high pressure

1. Introduction

Catalytic partial oxidation of methane (CPO) on a Rh-based catalyst is a promising syngas production route due to its autothermal, short space time operation [1]. The high reactivity and space velocity result in pronounced transport limitations that need to be explicitly accounted for during reactor and catalyst design. This work aims at proposing a reliable and comprehensive packed-bed reactor model to study the interplay between the chemical and physical phenomena occurring at CPO conditions on both particle and reactor scale.

2. Methods

The packed-bed reactor model explicitly accounts for external and internal diffusion limitations, among others by considering an interstitial and an intra-particle phase [1]. Axial diffusion of mass was assumed negligible due to the high gas velocity used. Energy balance equations were written in analogy to the mass balance, while for the solid phase, the axial conduction term was explicitly included. A microkinetic description for both surface reactions and homogeneous combustion [2,3] was applied to obtain detailed axial and pellet profiles for molecules, radicals and surface coverages. A set of second-order partial differential equations were written based on the above assumptions and discretized by applying orthogonal collocation with 6 and 11 points for interstitial and intraparticle coordinate and finite difference formula with 115 points unevenly distributed for reactor axial coordinate. With 32 gas phase species and 12 surface intermediates, a total number of 73,945 ODEs were formed and decoupled by implementing domain separation technique to improve numerical efficiency. Model simulations have been performed at typical CPO operation conditions, i.e., P_{tot} = 0.1–1.0 MPa, T_{in} = 773–1273 K, $W/F_{CH4,0}$ = 0.774 kg s mol^{-1}, $V/F_{tot,0}$ = $1.73 \cdot 10^{-4}$ m^3 s mol^{-1}, CH$_4$/O$_2$/N$_2$ = 2/1/4 (v/v/v), d_p = 0.4–1.2 mm, and validated against the available literature data [2].

3. Results and discussion

Significant gradients in both the interstitial and the intra-particle phase were observed for reactants and products, see Figure 1, indicating the reaction kinetics were severely limited by diffusion. This phenomenon was most pronounced at the reactor entrance zone where methane oxidation takes place, particularly for higher catalyst loading. Larger catalyst pellet size, and therefore larger distance between the pellets, enhanced both external and internal diffusion limitations, thus lowering the reactor performance and catalyst effectiveness. Homogeneous combustion became competitive to the surface reactions at pressure 1.0Mpa, redirecting the overall reaction path towards total oxidation in the reactor entrance region. H$_2$O was further consumed on the catalyst surface via steam reforming reactions maintaining the H$_2$ production, while CO$_2$ consumption was not favoured on Rh catalyst due to the low adsorption rate as simulated by the surface

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kinetics applied in this work [2], resulting in a decrease of overall CO selectivity, see Table 1. The solid temperature rise was slightly lowered at the reactor entrance region by introducing the axial conduction term, with little effect on the overall reactor performance.
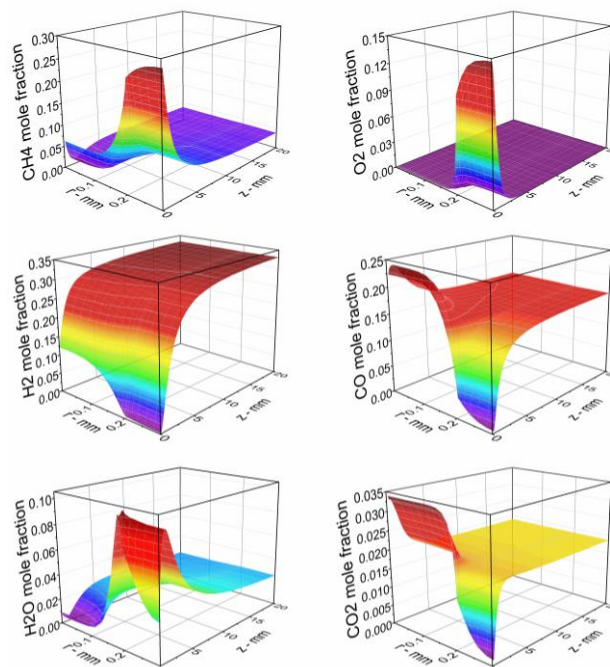

Figure 1. Mole fraction profiles for molecules ($P_{tot} = 0.1$MPa, $T_{in} = 773$K, $W/F_{CH4,0} = 0.774$ kg s mol^{-1}, $V/F_{tot,0} = 1.73 \cdot 10^{-4}$ m^3 s mol^{-1}, $CH_4/O_2/N_2 = 2/1/4$ (v/v/v), $d_p = 0.4$mm. r – pellet coordinate, r = 0 – 0.2mm: intraparticle phase, r = 0.2 – 0.297 mm: interstitial phase, z – axial coordinate)

Table 1. CH_4 conversion and syngas selectivity at elevated pressure.

Pressure (MPa)	0.1	1.0	1.5	2.0	2.5	3.0
CH_4 conversion	0.751	0.830	0.828	0.824	0.818	0.813
H_2 selectivity	0.796	0.816	0.818	0.822	0.822	0.819
CO selectivity	0.885	0.876	0.860	0.835	0.811	0.792
H_2/CO	1.80	1.86	1.90	1.97	2.03	2.07

4. Conclusions

A comprehensive reactor model suitable for investigating CPO reactions was proposed and validated. The modelling results confirmed the reactor performance was highly determined by diffusion phenomena and, hence, to a lesser degree influenced by catalyst loading while largely impacted by catalyst size. At high pressure from 1.0Mpa, homogeneous combustion becomes important and changes the reaction path, producing more CO_2.

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